DIRECTIONAL MODIFYING OF INORGANIC OXIDES SURFACE BY CATALYTIC ACTIVE COMPLEXES OF COBALT WITH 1,3-DIAZOLES

L.A. Belyakova [1] and V.M. Linkov [2]

[1]*Institute of Surface Chemistry, National Academy of Sciences*
Gen. Naumov str. 17, Kyiv-164, 03680 UKRAINE, e-mail: v-bel@mail.kar.net
[2]*Department of Chemistry, University of the Western Cape*
Bellville 7535, Republic of SOUTH AFRICA

Abstract

In this study a technique for the surface modification of ceramic membranes, consisting of 70 % Al_2O_3 and 30% ZrO_2 by disperse silica and complexes of cobalt with 1,3-diazoles has been developed. This was done by first reacting them with silica and then with γ-aminopropyltriethoxysilane, cyanuric chloride (or 1,10-diiododecane) and 1,3-diazole (imidazole or histamine). Heterogenized cobalt complexes with 1,3-diazoles, grafted onto the membrane surfaces, were obtained. It was established that the cobalt complexes with 1,3-diazoles had a deformed tetrahedral structure and it was only the nitrogen atoms of the grafted heterocycles of imidazole which were involved in the formation of four co-ordinate metal complexes. The catalytic activity of the produced membranes in the reaction of the liquid phase oxidation of cumene by molecular oxygen under mild conditions (atmospheric pressure and a temperature less than 100 °C) has been demonstrated. A study of the oxidation mechanism revealed that the reaction proceeds via the formation of oxygenated complexes of 1,3-diazoles with cobalt ions on the catalytic membrane surface. The formation of radicals takes place due to the oxygenation of heterogenized cobalt complexes, according to the following reaction: $O_2 \cdot Co(II) \rightarrow O_2^- \cdot Co(III)$. The catalytic reaction of cumene oxidation proceeds with the participation of Co(III)-catalysts according to a mechanism involving electron transfer. The newly developed method for the preparation of catalytic membranes can also be used for the manufacturing of selective ceramic membranes with hydrophobic or hydrophilic surfaces.

The present study deals with the preparation of catalytic, ceramic-based membranes, useful for the oxidation of organic substances. There is a serious need nowadays to conduct such processes under mild conditions, as under such conditions it is possible to synthesize many important organic substances. It can be expected that a highly effective catalytic membrane could be developed if a catalyst, which is active in oxidation under mild conditions, was to be introduced into the ceramic membrane matrix. Accurate selection of the catalytic phase and the appropriate ceramic membrane support were pre-requisites for the preparation of such catalytic membranes.

It is known from the literature [1] that silica can be used for the preparation of membranes as it is possible to obtain stable sols and gels from it [2]. It is also the main component of industrially produced porous glass membranes [1,3]. The surface chemistry of silica has been better-studied [4-6] than that of other oxides of multivalent metals which are used in production of ceramic membranes, for example, zirconium-, titanium- and cerium oxides. The properties of silica can be drastically changed by grafting with different organic, silicon organic or co-ordinate compounds [6-9]. If silica is present in the ceramic membrane matrix then its chemical modification can result in changes in the properties of

the inorganic membranes. For example, there could be an increase in membrane thermal and chemical stability, the membrane surface could be made hydrophobic and there could be controlled change in the pore sizes of the membranes. Chemical modification of membrane surfaces also provides a way in which catalytically active membranes can be prepared.

Complexes of 1,3-diazoles with transition metals are active in the oxidation, reduction, dehydration and hydroxylation reactions of organic compounds [10]. Therefore, the conversion of 1,3-diazoles into heterogeneous catalytic forms is of interest from two points of view, namely, for the synthesis of adsorptive and catalytic phases and for the modeling of active sites of biocatalysts [11,12]. It was assumed that inorganic membranes that were modified with complexes of transition metals with 1,3-diazoles would be catalytic active for the oxidation of organic compounds under mild conditions.

The aim of the present study was to investigate the possibility of preparing novel inorganic membranes that would combine the mechanical and chemical benefits of ceramics materials, the superior adsorption properties of silica and the high catalytic activity of complexes of transition metals with 1,3-diazoles. Such membranes would be useful in solving several important problems related with catalytic conversion of a variety of organic substances. Typical problems include catalytic decomposition of toxic compounds in aqueous solutions and fine organic synthesis.

The reaction of liquid-phase oxidation of cumene by molecular oxygen was used to demonstrate the catalytic properties of the new inorganic membrane materials. The latter were prepared by the impregnation of silica into ceramic membrane supports, followed by further modification with cobalt complexes with imidazole or histamine.

The chemical composition of the porous metal oxide ceramics was 70 % alumina and 30 % zirconia stabilized with yttria, their specific surface area was between 2 and 5 m^2/g, the average diameter of the pores was 0.2 μm and the total porosity was 45 %.

To ensure the optimal conditions for the grafting of metal complexes the surfaces of the membrane supports were modified, first by disperse silica and then by γ-aminopropyltriethoxysilane, 2,4,6-trichloro-1,3,5-triazine (or 1,10-diiododecane) and 1,3-diazole (imidazole or histamine) [9].

The metal complexes, chemically grafted onto the surface, were obtained as a result of contact of the modified membrane supports with 0.01-0.03 M solutions of $CoCl_2$ in acetone for 3 h at 25 °C.

A spectroscopic study of the structures of the heterogenized cobalt complexes with 1,3-diazoles was performed by means of UV-VIS spectrophotometer (PU 8800 Pye Unicam, England) in a diffuse reflection mode. For this purpose the standard attachment PU 7908/24 Integrating Spheroid was used.

The membranes modified by the cobalt complexes with 1,3-diazoles were studied for their catalytic activity in the liquid phase oxidation of cumene. The catalytic activity was determined from the rate of oxygen absorption during the reaction, using volumetric equipment. The laboratory unit for testing catalytic activity comprised a glass reactor with a catalyst-containing ampoule, a pressure gauge and a system of vents for evacuation and oxygen supply. The unit was assembled on a platform that could be agitated. Oxygen at atmospheric pressure was used as the oxidizer. A constant reaction temperature was maintained by using a thermostat.

The experiments were carried out under the ex-kinetic condition with the cell shaking frequency exceeding 500 oscillations per min and over the temperature range 60-90 °C. Under these conditions the oxygen dissolution and mass transfer of reacting substances did not affect the reaction rate. The reaction kinetics data was obtained for the initial stage of the oxidation process where it was possible to ignore the influence of the reaction products on the reaction rate.

92

All cobalt complexes with 1,3-diazoles grafted onto the surfaces of modified membranes possessed catalytic activity in the liquid-phase oxidation of cumene. The heterogenized Co-complexes have a high chemical stability. They did not disintegrate upon heating up to 200-250 °C. The structure of the grafted cobalt complexes did not change upon contact with concentrated acetic acid and different solvents such as acetone, toluene and water, for 120 h at 25 °C.

The membranes modified by heterogenized cobalt complexes with 1,3-diazoles reversibly adsorbed molecular oxygen (the band of charge transfer ligand-metal $\pi^*O_2 \to \sigma^*Co$ from oxygen molecule to the central ion of Co-complex with the maximum at 25510 cm^{-1} [12,13]). It was expected therefore that such membranes would have high catalytic oxidation activity towards organic compounds. Four co-ordinate complexes of cobalt on the surfaces of the membranes modified by imidazole (or histamine) are identical and have a deformed tetrahedral structure [14]. It is only the nitrogen atoms of the grafted heterocycles of imidazole that are involved in the formation of metal complexes. The structure of these complexes is presented below.

L : Co(II) = 2 : 1

L : Co(II) = 1 : 1
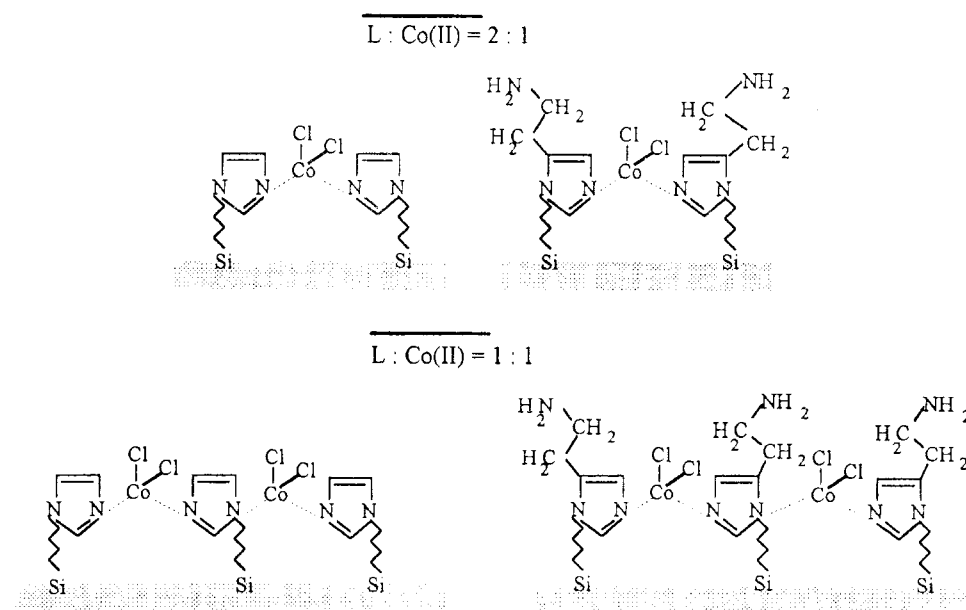
The deviations from the ratio L : Co(II) = 2:1 and 1:1 (Table 1) are caused by the simultaneous formation of both types of complexes.

The chemical structures of the obtained heterogenized metal complexes of 1,3-diazoles with cobalt resemble the structure of active centers of metal proteins. The study of the oxidation of organic substances under mild conditions, using such biocatalyst-mimicking ceramic-based membranes, was of special interest.

All the modified membranes (after modification by the cobalt complexes with 1,3-diazoles) possessed catalytic activity in the reaction of the liquid-phase oxidation of cumene at temperatures below 100 °C. Their structures remained unchanged upon contact with cumene and the oxidation products such as cumene hydroperoxide, acetophenone and dimethylphenylcarbinol. The reaction rate decreased with time (Fig. 1), but the regeneration of the catalyst was possible. At least six subsequent reaction-regeneration cycles were performed and a 100 % restoration of catalytic activity was observed in each case. The regeneration was achieved by passing argon at 150 °C and oxygen at room temperature through the reactor.

93

Table 1. Surface content of ligands and cobalt ions in catalytic membranes. Metal adsorption from 0.03 M solution (* - from 0.01 M solution)

Grafted ligand L	Surface content of ligand (μmol/m^2)	Co(II) (μmol/m^2)	Ratio L : Co(II)
Imidazole	2.9	1.5	1.9
	2.5	2.0	1.2
	2.5	1.4*	1.8
	2.4	1.5	1.6
	2.0	1.5	1.3
	2.0	1.2*	1.7
	1.2	1.2	1.0
	2.0	2.1	1.0
Histamine	2.0	1.4*	1.4
	1.6	1.6	1.0
	0.6	0.7	0.9

W , mm^3/ min

τ , min

Fig. 1. The rate of cumene oxidation at 65 °C in the presence of catalytic membranes:
1 - Imidazole : Co (II) = 1.8;
2 - Histamine : Co (II) = 0.9

It was found that the catalytic membranes obtained by the impregnation of cobalt chloride onto non-modified ceramic membrane supports possessed much lower catalytic activity in the reaction of cumene oxidation and this decreased irreversibly with time. The dependence of oxygen absorption V_{O_2} on the reaction temperature, shown in Fig. 2, confirmed the participation of heterogenized Co-complexes in the reaction of the liquid-phase oxidation of cumene.

The method of joint initiation was applied for the clarification of the mechanism of the reaction of cumene oxidation in the presence of membrane-supported complexes of cobalt with imidazole (or histamine). Cu-silica gel prepared by ion exchange was used as co-initiator. It is known that Cu-silica gel is involved in cumene oxidation only at the stage of chain formation in the radical-chain process [15]. Experimentally obtained (W^{exp}_{cum}) and calculated (W^{calc}_{cum}) cumulative rates of cumene oxidation in the presence of the membrane-supported cobalt complex with imidazole and Cu-silica gel are given in Table 2. The total rate of cumene oxidation was calculated from the formula

$$W_{cum} = (W^2_{Cu^{2+}/SiO_2} + W^2_{Co\text{-}imidazole})^{1/2}$$

where W_{Cu^{2+}/SiO_2} - the rate of cumene oxidation in the presence of Cu-silica gel; $W_{Co\text{-}imidazole}$ - the rate of cumene oxidation in the presence of a cobalt complex with imidazole.
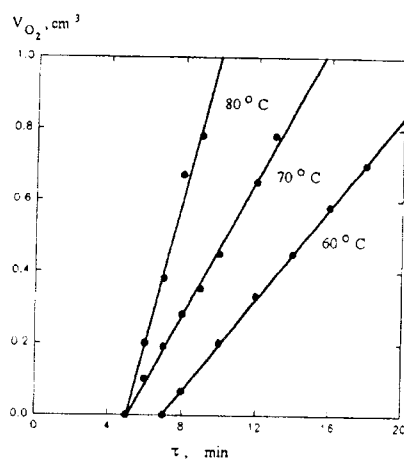
94

V_{O_2}, cm³

τ, min

Fig. 2. The kinetics of oxygen absorption during cumene oxidation in the presence of the catalytic membrane at 60-80 °C (10 mg catalyst, Histamine : Co(II) = 0.9)

The dependence of the reaction rate on the mass of imidazole-containing catalytic membranes present in the reactor (q) is given in Fig. 3. The reaction rate initially increased with an increase in the amount of the catalyst and then reached a constant value. If plotted in co-ordinates $W = f(q^{1/2})$ then the relationship was linear. Similar results were obtained with histamine-containing catalytic membranes. Based on the above mentioned findings it was concluded that the process of cumene oxidation in the presence of cobalt complexes with 1,3-diazoles grafted on the surface of modified membranes took place according to a radical-chain mechanism. The involvement of the catalyst was limited to the first stage of radical formation only.

The introduction of carbon with a pre-oxidized surface as an inhibitor of the radical formation process lead to a decrease in the cumene oxidation rate (Fig. 4) and testified to the participation of the radicals in the reaction mechanism. The appearance of these radicals is either due to the decomposition of cumene hydroperoxide or to the activation of molecular oxygen. As can be seen from Fig 5, replacement of oxygen with air did not affect the kinetics of cumene oxidation in the presence of Cu-silica gel. It was assumed therefore that in this case the radicals were formed due to the hydroperoxide decomposition. A similar replacement in the case of catalytic membranes modified by Co-complexes with 1,3-diazoles resulted in a significant decrease in the cumene oxidation rate, which was completely restored when pure oxygen was used again. These results testify to the existence of two different reaction mechanisms that play a role in the presence of the Cu-silica gel catalyst and catalytic membranes containing Co-complexes with 1,3-diazoles. Apparently, the ability of Co-complexes to form oxygenated intermediates plays a major role in the latter case.

Table 2. Rates of cumene oxidation (experimentally obtained W^{exp}_{cum} and calculated W^{calc}_{cum}) at simultaneous presence of Cu-silica gel and ceramic membrane modified by Co-complex with imidazole (ratio Imidazole : Co(II) = 1.6)

Amount of catalyst q (mg/l)	$W^{exp}_{cum} \cdot 10^7$ (mol/l·s)	$W^{calc}_{cum} \cdot 10^7$ (mol/l·s)
5.0	1.5	1.4
10.0	1.9	1.8
20.0	2.2	2.0

This assumption was confirmed by a study of the kinetics of oxygen absorption by deoxygenated Co-complexes (Fig. 6). The deoxygenation was carried out by heating the catalyst and the substrate in argon (curve 2) and oxygen (curve 3) up to the boiling point of cumene (152-153 °C). A reduction in the cumene oxidation rate was observed in both cases. In an attempt to explain the above mentioned phenomenon it was suggested that the oxygen activation equilibrium $O_2 \cdot Co(II) \leftrightarrow O_2^- \cdot Co(III)$ which prevailed on the catalytic membrane surfaces was no longer present at elevated temperatures due to
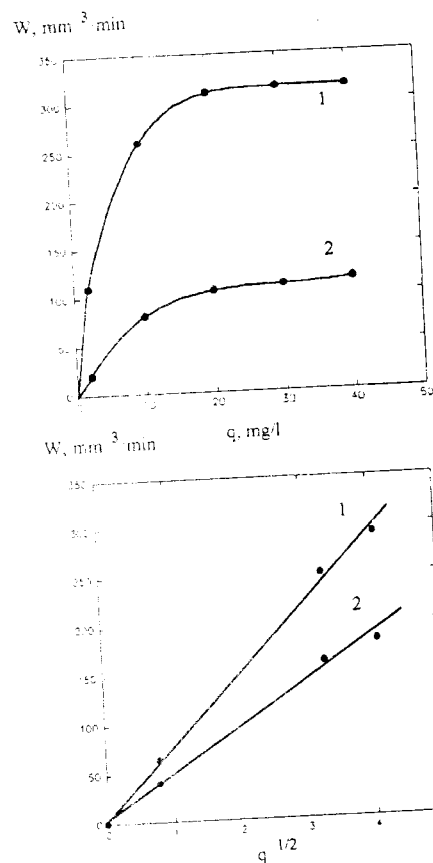
Fig. 4. Effect of carbon with oxidized surface on the kinetics of oxygen absorption V_{O2} during cumene oxidation in the presence of catalytic membranes with a ratio Histamine : Co(II) = 0.9 (60 °C, 10 mg catalyst): 1 - without adding oxidized carbon; 2-4 - with the addition of 20, 35 and 50 mg of oxidized carbon respectively

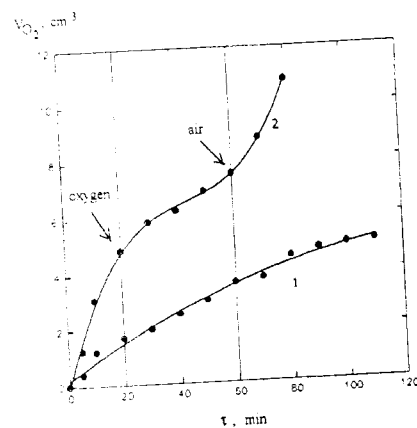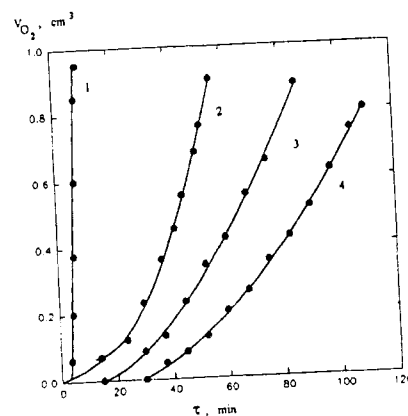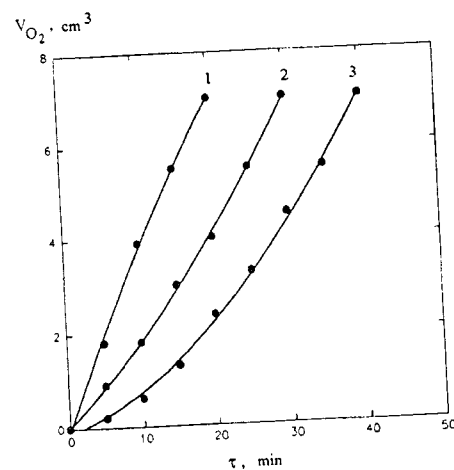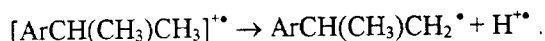**Fig. 3.** The rate of cumene oxidation at different relative concentrations of the membrane catalyst (60 °C, ratio Imidazole : Co(II) is 1.6 and 1.0 - curves 1 and 2 respectively)

Fig. 6. The effect of deoxygenation on the kinetics of oxygen absorption V_{O2} during cumene oxidation in the presence of the catalytic membrane with a ratio Histamine : Co(II) = 0.9: without deoxygenation (1), deoxygenation in argon atmosphere (2) and oxygen atmosphere (3)

Fig. 5. Kinetics of oxygen absorption V_{O2} during cumene oxidation in the presence of Cu-silica gel (1), and the catalytic membrane with a ratio Histamine : Co (II) = 0.9
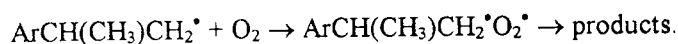
removal of oxygen from the surface of the catalyst. Restoration of the catalytic properties took place when the equilibrium was restored and an adequate quantity of Co(III) was present. Apparently, the initial formation of cation-radicals on the Co(III)-membrane catalysts is analogous to the process of oxidation of alkylaromatic compounds in the presence of homogenous Co(III)-catalysts [16]:
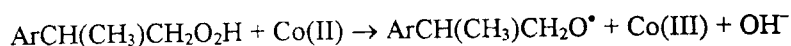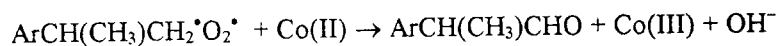
$$ArCH(CH_3)_2 + Co(III) \rightarrow [ArCH(CH_3)CH_3]^{\cdot+} + Co(II).$$
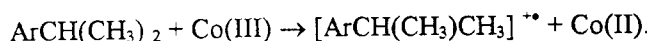
The loss of a proton takes place as follows:

$$[ArCH(CH_3)CH_3]^{\cdot+} \rightarrow ArCH(CH_3)CH_2^{\cdot} + H^{\cdot+}.$$

In the presence of oxygen the following reaction takes place:

$$ArCH(CH_3)CH_2^{\cdot} + O_2 \rightarrow ArCH(CH_3)CH_2^{\cdot}O_2^{\cdot} \rightarrow products.$$

The catalyst is regenerated by means of the following reactions:

$$ArCH(CH_3)CH_2^{\cdot}O_2^{\cdot} + Co(II) \rightarrow ArCH(CH_3)CHO + Co(III) + OH^-$$

$$ArCH(CH_3)CH_2O_2H + Co(II) \rightarrow ArCH(CH_3)CH_2O^{\cdot} + Co(III) + OH^-$$

The oxidation process did not proceed according to the conventional mechanism (via the decomposition of cumene hydroperoxide) but by way of the primary oxidation of Co(II) to Co(III) by molecular oxygen, followed by the participation of Co(III) in the formation of the cation-radicals.

References

1. Brave R.R. Inorganic Membranes: Synthesis, Characteristics, and Applications. New York: Van Nostrand Reinhold, 1991. 750 p.
2. Iler R.K. The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica. New York: John Wiley and Sons, 1979. 1008 p.
3. Schnabel R., Vaulont W. High-pressure Techniques with Porous Glass Membranes // Desalination. - 1978. - V. 24, N 1. - P. 249-272.
4. Linsen B.G. Physical and Chemical Aspects of Adsorbents and Catalysts. London-New York: Academic Press, 1970. 580 p.
5. Kiselev A.V. and Lygin V.I. Infrared Spectra of Surface Compounds (in Russian). Moscow: Nauka, 1972. 459 p.
6. Vansant E.F., Van Der Voort P., Vrancken K.C. Characterization and Chemical Modification of the Silica Surface. Amsterdam: Elsevier, 1995. 555 p.
7. Unger K.K. Porous Silica, Its Properties and Use as Support in Column Liquid Chromatography. Amsterdam: Elsevier, 1979. 350 p.
8. Chuiko A.A., Gorlov Yu.I. Chemistry of Silica Surface (in Russian). Kiev: Naukova Dumka, 1992. 248 p.
9. Tertykh V.A., Belyakova L.A. Chemical Reactions with Participation of Silica Surface (in Russian). Kiev: Naukova Dumka, 1991. 264 p.
10. Enikolopyan N.S. Porphyrins: Spectroscopy, Electrochemistry, Application (in Russian). Moscow: Nauka, 1987. 384 p.
11. Burwell R.L. Modified Silica Gels as Adsorbents and Catalysts // J. Chem. Technol. - 1974. - V. 4, N 6. - P.370-377.

12. Preparation and Investigation of Cobalt Complexes Grafted to Surface of Aerosil / T.N.Yakubovich, Yu.I.Bratushko, K.B.Yatsimirskii, V.I.Bogomaz, L.I.Sologub, A.A.Chuiko // Adsorption and Adsorbents (in Russian). –1984.- N 12. - P.55-60.

13. Lever A.B.P., Gray H.B. Electronic Spectra of Metal Dioxygen Complexes // Accounts Chem. Res. - 1978. – V. 11, N 9. P. 348-355.

14. Lever A.B.P. Inorganic Electronic Spectroscopy. Amsterdam: Elsevier, 1984. 420 p.

15. Evmenenko N.P., Gorokhovatskii Ya.B., Tsepalov V.F. Investigation of Kinetics and Mechanism of Cumene Oxidation // Petroleum Chemistry (in Russian). – 1970. – V. 10, N 2. – P. 226-230.

16. Masters C. Homogeneous Transition-Metal Catalysis. London-New York: Chapman and Hall, 1981. 285 p.